

MR. SERGIO MARTINEZ-MARTINEZ (Orcid ID : 0000-0001-7628-8934)

MR. LUIS PÉREZ VILLAREJO (Orcid ID : 0000-0002-6912-9844)

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Mail id: sergiomartmart@gmail.com

New waste-based clinkers for the preparation of low energy cements. A step forward towards Circular Economy

Sergio Martínez-Martínez¹, Luis Pérez-Villarejo¹, Dolores Eliche-Quesada¹, Pedro J. Sánchez-Soto², Angeliki Christogerou^{3,4}, Dimitra G. Kanellopoulou^{3,4}, George N. Angelopoulos^{3,4}

¹Department of Chemical, Environmental and Materials Engineering, University of Jaén, Campus “Las Lagunillas”, Jaén, Spain.

²The Institute of Materials Science (ICMS), Spanish Council of Scientific Research (CSIC), c/Américo Vespucio 49, Sevilla, Spain.

³Department of Chemical Engineering, University of Patras, Caratheodory 1, University Campus, Patras, Greece.

⁴INVALOR: Research Infrastructure for Waste Valorization and Sustainable Management, Caratheodory 1, University Campus, Patras, Greece.

Abstract

This paper describes the use of industrial wastes arising from different production processes of the ceramic and marble industries as raw materials for the design and formulation of new cement clinkers with a high content of dicalcium silicate (Belite). The aim is to reintroduce these wastes in the industrial sector and take advantage of them for a greater environmental benefit, as indicated by the principles of the circular

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economy. Formulations containing 2.5, 5 and 10 wt.% of chamotte and marble sludge respectively and a waste-free formulation have been designed to obtain clinkers with a content of dicalcium silicate higher than 60 wt.%. The different blends have been studied up to a maximum temperature of 1390 °C by Thermal Analysis. Other techniques such as XRD, XRF, Modified Bogue Equation, Quality Indexes (LSF, AM, SM) and Optical Microscopy have been used for the study and characterization of industrial wastes, the raw materials and the high belite-type cement dosages. The results indicate that this type of cements can be designed using different types of wastes and in this way reduce the environmental impacts caused by the extraction of raw materials and the deposition of the wastes in landfills, improving the circular economy of the construction industry.

Keywords: Industrial wastes; Chamotte; Marble sludge; High belite clinker; Circular economy

1. Introduction

Cement is one of the main building materials used in the world. One among many reasons of its wide use is its durability and compatibility with other elements allowing the manufacture of composite materials with better properties. The cement manufacturing industry is one of the main industrial sources for the atmospheric emissions of greenhouse gases (GHG), which are contributing in part to the process of climate change that currently plagues our planet. Global cement production has increased more than 30-fold since 1950 and almost 4-fold since 1990, with much more rapid growth than global fossil energy production in the last two decades. Since 1990 this growth has largely been observed because of rapid development in China where cement production has grown by a factor of almost 12 such that 73 % of global growth in cement production since 1990 occurred in China.^{1,2} Total emissions from the cement industry could therefore contribute as much as 8 % of global CO₂ emissions.²

In particular, the Spanish cement industry produced around 22.5 million tonnes of cement in 2018, which represents only 60 % of the total capacity and generates more than 4,000 direct and 12,000 indirect jobs.³ Taking into account an average of 0.83 tonnes of CO₂/tone of cement,⁴ it results that the cement sector contributes 18.68 million tonnes of CO₂ annually. However, studied cases have shown that a 9 % reduction in CO₂ production is feasible in the case of waste utilization.⁵⁻⁷

In 2016, greenhouse gas emissions in the EU-28 decreased by 22 % compared with 1990 levels, representing an absolute reduction of 1 279 million tonnes of CO₂-equivalents. It put the EU on track to surpass its 2020 target, which is to reduce GHG emissions by 20 % by 2020 and by 40 % by 2030 compared with 1990.⁸

Belite Portland Cements (BPC) or belite cements compared to OPC (Ordinary Portland Cement) have an increased content in belite mineral than alite. The result is the reduction of CO₂ emissions by two

ways: lower energy consumption due to lower firing temperature, and reduced content / consumption of limestone. The energy demand is estimated at 15-20 % less, for a Lime Saturation Factor of 80-85 %.⁹⁻¹¹ An important advantage of those alternative formulations is that it can help the cement industry to reduce its GHG emissions in the manufacturing process and thus reduce the impact on the environment caused by the production of OPC clinker.¹²⁻¹⁵ The biggest disadvantage of belite (C_2S) rich cement is the slow rate of hydration.⁴

In addition, the increase of industrial activity generates wastes that treated properly and depending on their chemical composition, can generate numerous alternatives to current raw materials used in the industry of cement production (clay and limestone). Currently, the majority of the waste generated in the mining industry or in the materials construction industry is deposited in landfills. This generates numerous environmental problems and increased cost demands for the respective companies. The reuse of wastes by means of circular economy is defined as: "A circular economy aims to maintain the value of products, materials and resources for as long as possible by returning them into the product cycle at the end of their use, while minimising the generation of waste. The fewer products are discarded, the less material will be extracted, improving our environment. This process starts at the very beginning of a product's lifecycle: smart product design and production processes can help save resources, avoid inefficient waste management and create new business opportunities".¹⁶ In 2015, the European Commission adopted an ambitious 'Circular Economy Package'. An EU Action Plan for the circular economy establishes a concrete programme of actions outlining measures that cover the entire product life cycle: from production and consumption to waste management and the market for secondary raw materials.¹⁶

Clinker is the main component of cement, which is obtained by mixing raw materials such as limestone and clays and firing them at temperatures close to 1500 °C for OPC. The main phases in the Ordinary Portland Cements are: alite ($3CaO \cdot SiO_2$, C_3S), belite ($2CaO \cdot SiO_2$, C_2S), tricalcium aluminate ($3CaO \cdot Al_2O_3$, C_3A), and tetracalcium aluminate ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, C_4AF).¹⁷ In the case of OPC clinker, which is currently the most commonly used type of cement, the silicates account for 60-80 wt.% of the components, alite is the highest proportion and belite is the smallest proportion. A typical mineralogical composition of a OPC clinker consists of 60 wt.% C_3S , 20 wt.% C_2S , 6 wt.% C_3A , 12 wt.% C_4AF and 2 wt.% of minor components.¹⁸ The new type of eco-cement clinker studied is based mainly on the reversal of the alite-belite ratio, taking into account the new proposed dosages with belite content between 60-65 wt.%. The expected results will lead to a decrease in firing temperature (maximum clinkering temperature is 1390 °C), and therefore to a lower amount of fuel in the manufacturing process, all of which leads to a reduction in GHG emissions.¹⁹

In the ceramic industry there is distinction between traditional ceramics and technical ceramics. Traditional ceramic materials are based on the firing of clays at different temperatures, depending on the characteristics required to obtain, on a large scale, with the main manufactured products being construction bricks, pavers, tiles, ceramic boards, etc. One of the main residues generated in the production of these ceramic products are broken pieces, cracked, with superficial defects and / or badly fired. This type of ceramic elements can be subjected to mechanical processes to reduce their particle size distribution and, currently, a large percentage of their production is deposited in controlled landfills. Crushed fired ceramics and particles of small particle size distribution can be called as "chamotte". Therefore, it is a solid waste that is produced during the manufacture of ceramic pieces.²⁰ One of the main characteristics of the chamotte is that it can be used as a non-plastic in ceramic pastes, since they reduce the excessive plasticity of some clays by not retaining as much water. The chamotte has the characteristic of not contracting when mixed, since being fired clay, in the firing process has lost all its constitution water. According to Directive 2008/98 / EC on waste ('Waste Framework Directive' or 'WFD')²¹ and Commission Decision 2000/532 / EC on the list of waste ('List of Waste' or 'LoW'), as revised in 2014 and 2017,²² the LER code in which the chamotte can be classified is within the group "10 12 wastes from manufacture of ceramic goods, bricks, tiles and construction products", specifically with the code "10 12 08 waste ceramics, bricks, tiles and construction products (after thermal processing)".²³

Marble is a metamorphic carbonate rock that is composed mainly of calcite and/or dolomite in a percentage that exceeds 90 %. The main marble producing countries in the world are Italy, China, Iran, Turkey and Spain.²⁴ For the process of extracting quarry marble blocks, methods such as the use of explosives or the use of diamond wire rope cutters are used. These methods basically consisting of a steel wire with diamond powder, which by means of a friction process with the rock cut it until obtaining the block with the desired or allowed dimensions according to the type of deposit. Once the marble block has been extracted, it is cut through large-diameter diamond discs to obtain marble slabs. It is estimated that during the process of cutting blocks to produce 20 mm thick boards, 20-25 wt.% of the mass of the block is lost in the form of waste.²⁴ Finally, the polishing process of the marble slabs is carried out. It is estimated that, during the polishing process of the tables, approximately 0.2 cm of thickness is lost from each table.²⁴ During all the process indicated from the extraction of the marble block in the quarry to the final treatment of the marble boards and their sale, two types of inert wastes are generated: the cuttings and sludge ones. The cuts are larger fragments, which are generally reused for the manufacture of construction aggregates. In the case of sludge, these are usually disposed off in landfills controlled after the process of separating the water from the process previously indicated in evaporation ponds or by press filters, obtaining an approximate ratio of 80 % fine particles and 20 % water. The production of dry waste corresponds to approximately 200 kg per cubic meter of treated marble.²⁴ According to Directive 2008/98 / EC on waste

('Waste Framework Directive' or 'WFD')²¹ and Commission Decision 2000/532 / EC on the list of waste ('List of Waste' or 'LoW'), as revised in 2014 and 2017,²² the LER code in which the sludge marble can be classified is within the group "01 04 wastes from physical and chemical processing of non-metalliferous minerals ", specifically with the code "01 04 13 wastes from stone cutting and sawing other than those mentioned in 01 04 07".²³ Different authors have studied the possibility of introducing in the formulation of new types of cement wastes that are generated in mining and material processing industries.^{4,12-15,17,19,20,25-38}

In this research, industrial wastes, such as chamotte and marble sludge were investigated as possible raw materials for the design of the new high belite cements. Depending on the chemical composition of the wastes, they can totally or partially replace the raw materials used in the cement industry (clays and limestone). In general, all materials of mineral origin or industrial by-products that contain the main components of lime, silica, alumina and iron oxide can be used as potential raw material for the production of cement clinkers.³⁹

2. Experimental procedures

Four raw materials and two types of wastes have been selected and characterized to design and produce the different dosages. The limestone has been provided by the company ARIDOS ANAYA, S.L., from Castellar (Jaén), the red, black and yellow clays by the company ARCILLAS BAILEN, S.L., from Bailén (Jaén), the chamotte waste by the company LADRILLOS BAILEN, S.A., from Bailén (Jaén), and the marble sludge comes from Cehegín (Murcia). All raw materials were received in the laboratory and homogenized. The three types of clays were received directly from the mining operation without prior classification, so the size of them was very heterogeneous. The limestone corresponded to a fraction of size 4-6 mm. The received chamotte corresponded to fragments of different sizes of ceramic pieces sintered at 950 °C as wastes with various defects (cracks, heterogeneously fired zones, etc.). The marble sludge corresponded to dry residue that was going to be deposited in a landfill with a very homogeneous fraction of less than 0.15 mm. All raw materials were dried in a laboratory oven (at 105 °C until constant weight) and subsequently ground in a planetary ball mill until a particle size of less than 0.90 mm was obtained. The control of the particle size is important because it influences the physical and mechanical characteristics of the final product.⁴⁰

The characterization of raw materials and wastes includes chemical composition, determined by X-ray fluorescence (XRF, Philips Magix Pro XRF model PW-2440), mineralogical composition by X-ray diffraction (XRD, X ' PANALytical PERT PRO) and thermal analysis by Differential Scanning Calorimetry/Thermogravimetry (DSC/TG) (NETZSCH STA 449F3 JUPITER) and NETZSCH Proteus interpretation software.

For the design of clinker compositions, a spreadsheet was built using Microsoft Excel® software. Based on the results obtained from the characterization of raw materials, the mineralogical phases formed are estimated according to the study of the Bogue Equations. The limits determined were imposed by the indexes: Lime Saturation Factor (LSF), which is the ratio of CaO to the other three main oxides, Aluminum Modulus (AM) and the Silica Modulus (SM).⁴ The Bogue equations used are the following:

- $C_3S = 4.0710 \cdot CaO - 7.6024 \cdot SiO_2 - 1.4297 \cdot Fe_2O_3 - 6.7187 \cdot Al_2O_3$
- $C_2S = 8.6024 \cdot SiO_2 + 1.0785 \cdot Fe_2O_3 + 5.0683 \cdot Al_2O_3 - 3.0710 \cdot CaO$
- $C_3A = 2.6504 \cdot Al_2O_3 - 1.6920 \cdot Fe_2O_3$
- $C_4AF = 3.0432 \cdot Fe_2O_3$

The equations used to calculate the indexes, Lime Saturation Factor (LSF), the Aluminum Modulus (AM) and the Silica Modulus (SM), are the following:

- $LSF = (100 \cdot CaO) / (2.8 \cdot SiO_2 + 1.18 \cdot Al_2O_3 + 0.65 \cdot Fe_2O_3)$
- $AM = Al_2O_3 / Fe_2O_3$
- $SM = SiO_2 / (Al_2O_3 + Fe_2O_3)$

In this investigation, the main objectives in the design of the dosages are to obtain high belite clinkers with different amounts of C_2S , C_3S , C_4AF and C_3A . Specifically, chemically adjusted mixtures of clinker with a quantity of belite greater than 60 wt.% and an amount of 9-14 wt.% alite have been formulated, as well as maintaining the LSF in the range of 77-80 %, specific to belite cements⁴ with the objective of obtaining high quality hydraulic cements. Seven clinkers were prepared: one reference clinker without wastes (WST_0), three with 2.5, 5 and 10 wt.% chamotte called CMH_2.5, CMH_5 and CMH_10 respectively and finally three clinkers with 2.5, 5 and 10 wt.% marble sludge named as MRB_2.5, MRB_5 and MRB_10 respectively. The mineralogical phases according to the Bogue equations and the specific limits of cement (LSF, AM, SM) are presented in Table 2.

The different blends were prepared by mixing the raw materials and homogenized waste as previously designed, proceeding to the preparation with a minimum water addition of the spherical pellets (approximate diameter of 15-20 mm) by hand.²⁶ These pellets were dried in a laboratory oven at 110 °C to eliminate the added moisture.

The dry pellets were placed in a magnesiachrome crucible and fired subsequently in a Nabertherm® HT 08/17 resistance furnace at different temperatures 1300 °C, 1330 °C, 1360 °C and 1390 °C with 40 min soaking time. Fast cooling of the fired pellets took place by simultaneously applying blown air and crushing by means of a hammer, for the stabilization of the most favourable structures of belite, the

alpha (α') and beta (β) and for the prevention of the gamma (γ) polymorph that has low or no hydraulic properties.^{4,26}

The produced clinkers stored in desiccators with silica gel, to prevent hydration. The crystalline phases were determined by XRD. For the optical observation, clinkers were mounted in epoxy resin, and polished by SiC papers to 4000 grit by using alcohol in order to avoid the hydration. Surface was etched with aqueous solution of Nital 1 % for 10 sec.

3. Results and discussions

3.1. Raw materials and wastes

The chemical composition of the raw materials and industrial wastes are shown in Table 1 (expressed as oxides). The clays are composed mainly of SiO_2 , highlighting the content in K_2O and MgO of the red clays, as well as the highest content in CaO , Al_2O_3 and Fe_2O_3 of the black and yellow clays. The limestone is constituted mainly by CaO , although its high MgO content stands out, which will be confirmed by the thermal analysis and demonstrates the presence of the dolomite phase observed by XRD. The chamotte is characterized by a high content of SiO_2 , in addition to important contents of CaO and Al_2O_3 (Figure 1). The marble sludge is practically entirely made up of CaO , presenting a very important loss of ignition (Table 1).

Table 1.

Figure 1.

The phases identified by XRD analysis of the red clay are quartz, calcite and dolomite, muscovite (mica, illite) and hematite, being last responsible for the reddish color. The XRD pattern of the black clay identifies the presence of quartz, calcite and dolomite phases, hemihydrate gypsum (bassanite), chlorite, muscovite (mica, illite) and also rutile (TiO_2). In the XRD pattern of the yellow clay, the phases quartz, calcite and dolomite, muscovite (mica, illite), feldspars (albite and ortose) are identified. Finally, for the limestone, the phases identified by XRD are calcite and dolomite.

The phases identified by XRD in the chamotte waste (Figure 1) are quartz, calcite, hematite, anhydrite, mica (dehydroxylated muscovite, illite), feldspar, orthose and anorthite (calcium aluminosilicate), which is the product of the thermal treatment. In the XRD pattern (Figure 1) of the marble sludge waste, only calcite is identified, which fits perfectly to the standard CaCO_3 form.

The DSC/TG analysis of the red, black and yellow clays (Figure 2a, b and c) shows an endothermic peak at temperatures between 0-200 °C which demonstrates the elimination of weakly bound water (dehydration). In the temperature range between 200-600 °C a weight loss attributed to the removal of

organic matter and dehydroxylation of the silicates is observed as indicated by the exothermic band centred at approximately 380 °C and the endothermic band centred at approximately 550 °C.^{41,42} The greatest weight loss occurs between 600-800 °C due to the decomposition of the carbonates as indicated by the endothermic peak centred at approximately 730-780 °C. At temperatures between 800-1100 °C an exothermic band associated with the crystallization of the high temperature phases is observed. At temperatures above 1100 °C, no weight loss is observed, showing the more pronounced endothermic DSC curve in the yellow clay that could possibly indicate the formation of a liquid phase.

Figure 2.

In the thermogravimetric curve (Figure 2d) of the limestone, composed of calcite and dolomite as indicated XRD analysis, a weight loss of 48 wt.% is observed up to 870 °C, which is due to the decomposition of the calcium and magnesium carbonates. According to the DSC analysis, the first endothermic reaction that occurs at 803 °C is due to the decomposition of carbonate ions associated with magnesium,⁴³ subsequently producing two other endothermic reactions at 845 °C and 860 °C, which are due to the decomposition of carbonate associated with calcium.⁴⁴⁻⁴⁷

In the thermogravimetric curve (Figure 2e) of the chamotte can be observed two important inflections that correspond in the first place to the weight loss due to the decomposition of the carbonates (4 wt.%) and a second weight loss between 1100 °C and 1200 °C (1.5 wt.%) due to the the formation of amorphous or vitreous phase. The weight loss can also be attributed to the amount of residual quartz that gradually decreases with temperature, taking into account the high SiO₂ content of the chamotte (Table 1), this phenomenon appears after 1150 °C, and also by the consumption produced by the ongoing reactions such as the formation of anorthite and mullite, other compounds such as illite and gehlenite decompose beyond 1150 °C. According to the DSC analysis, a first process of dehydration produced by heating can be observed as indicated by the endothermic reaction at a temperature lower than 100 °C, associated with the release of the absorption water. The second endothermic reaction at 575 °C is due to the transformation of the quartz from $\alpha \rightarrow \beta$. While the third endothermic reaction at 731 °C is due to the decomposition of calcite ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). Around 1100 °C an exothermic reaction is observed indicating the formation of crystalline phases. At temperatures above 1150 °C, no weight loss is observed, however, the DSC curve shows three endothermic peaks that could indicate the formation of a liquid phase. The thermogravimetric curve (Figure 2f) of the marble sludge waste shows a main inflection due to the decomposition of the carbonates with a weight loss of 44 wt.%. According to the DSC analysis, the presence of calcite is inferred through the endothermic reaction taking place around 866 °C.

3.2. Phase composition of synthesis of clinker

Table 2 summarizes the predicted phases and the target values as well as the indexes, according to the Bogue equations and the specific limits of cement.

Table 2.

Figure 3.

In the thermogravimetric curves of the various eco-cement clinkers blends manufactured (Figure 3) a common pattern in weight loss can be verified, which is indicated by the curve of the TG analysis, with a weight loss ranging from 37-39 wt.% up to a temperature of 870 °C approximately. In general, the weight loss produced at temperatures between 30-200 °C is due to the elimination of weakly bound water (dehydration). The endothermic band shown in the DSC analysis curves, with loss of weight at temperatures between 200-600 °C, are due to the elimination of organic matter and dehydroxylation of silicates, as can be seen in the analyses carried out for clay components (Figure 2a, b and c). The weight loss between 600-870 °C is due to the decomposition of the carbonates associated with magnesium and calcium, which can be seen in the analyses carried out on the limestone (Figure 2d). According to the DSC analysis, the first endothermic effect that takes place at approximately 770-800 °C, depending on the residue and the percentage added, is due to the decomposition of carbonate associated with magnesium,⁴³ subsequently producing two other endothermic reactions at temperatures between 830 °C and 865 °C, which are due to the decomposition of carbonate associated with calcium of calcite.⁴⁷ From 1050 °C and up to 1200 °C different reactions can be observed that are due first to the combination of CaO and SiO₂ to form the belite phase, as well as to the combination of CaO with Al₂O₃ and Fe₂O₃ to form tetracalcium aluminate ferrite. Subsequently, at temperatures above 1200 °C, the reactions of combination of CaO with SiO₂ to form alite and CaO with Al₂O₃ to form tricalcium aluminate are produced.

In the XRD analysis (Figure 4) of different clinkers can be observed a common pattern independent of the raw material and waste composition. This is because the chemical composition is similar to all clinkers. On the clinkers fired at 1300 °C and 1330 °C, that also show a common pattern, identified phases are alite (C₃S), α'- and β - belite (C₂S), γ - belite (C₂S), tricalcium aluminate (C₃A), tetracalcium aluminate ferrite (C₄AF) and periclase. As indicated above, γ - C₂S polymorph has no hydraulic activity, so this is not good for the future cement properties. The XRD pattern of the clinkers fired at 1360 °C and 1390 °C identifies a common pattern with the presence of alite (C₃S), α'- and β - belite (C₂S), tricalcium aluminate (C₃A), tetracalcium aluminate ferrite (C₄AF) and periclase. These results indicated that the temperature must be greater than 1330 °C for the formation of the belite polymorphic forms that have a good hydraulic activity (α'- and β - C₂S).

Figure 4.

Figure 5.

The microstructures of the calcined clinkers at 1390 °C were observed on polished sections (etched with nital 2 %) and recorded by reflected light microscope (Figure 5). A predominantly zone with belite crystals is observed in all samples, with irregular to normally rounded-shaped grains (red circles). Euhedral to subhedral alite blue crystals of different sizes can be distinguished (blue circles). This is normal because on the design of the blends (Table 2) more than 10 % of alite was calculated. Also some molten phases can be distinguished between belite round grains with numerous pores at 200X micrographs (Figure 5a, b and c). The distribution of the porosity depends on the firing temperature, the composition of the clinker, the particle size distribution of the blend and the type of furnace.⁴⁸ The molten phase that is between the belite grains is mainly constituted by the ferrite and aluminate phases, which do not occur individually due to the difficulties imposed by their microcrystalline texture. We know their composition based on the results of the design through the Bogue equations. A colourless grain of periclase (magnesium oxide) can be distinguished on Figure 5d at 500X for the micrograph of control clinker calcined at 1390 °C (yellow circles). On Figure 5d, e and f free lime is observed like rounded colourless grains as inclusions on alite grains (green circles).

Due to the rapid cooling to which the eco-cement clinker is subjected by forced air flow and clinker breakage by hammer, in order to stabilize the belite in the polymorphic phases α' - and β - C_2S and avoid the formation of γ - C_2S , it is promoted that the transitions of the belite polymorphism occur successively. It leads to the formation of a complex microstructure due to twinning or exsolution within the crystals. Belite grains are generally round in shape, blue in color due to the type of engraving and parallel crossed streaks.^{4,49}

4. Conclusions

From the XRD results and the optical observation of the micrographs it is evident that the formation of the desired mineralogical phases is in agreement with the estimated phases from the Bogue equations. The produced clinkers predominantly contain well-formed belite and alite crystals. This indicates that the partial replacement of raw materials with industrial wastes and the reduction on the firing temperature for the clinker production is feasible. Moreover, the presence of α' - and β - C_2S polymorphic forms of belite on the XRD patterns of the clinkers agree with the method used by which rapid cooling was applied in order to stabilise the desired mineralogical phases. According to the XRD patterns it is necessary a highest temperature than 1330 °C to avoid the formation of γ - C_2S . The presence of periclase grains in the microstructure of the clinkers are in agreement with the XRD results and the characteristic peaks observed which is mainly attributed to the chemical composition of limestone and the increased MgO content.

The production of high belite cements with chamotte and marble sludges is feasible and can offer significant environmental advantages. There are numerous types of industries that generate industrial wastes that, due to their chemical composition, can be used as raw materials in the calculation of dosages and the manufacture of cements, avoiding their deposit in controlled landfills or uncontrolled dumping, taking into account the concept of circular economy. The need for a lower quantity of raw materials to be extracted from nature for the manufacture of cements and the use of industrial waste reduces the carbon footprint of the cement industry.

The manufacture of cement clinker with a high content of belite, due to the lower amount of energy required by the lower clinkerization temperature compared to Ordinary Portland Cements, as well as the use of chamotte and block cut and marble table polishing sludge and as a substitute for raw materials (clays and limestone) leads to lower CO₂ emissions for the cement industry.

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Figure 3. DSC (green line)-TG (red line)-DTG (blue line) analysis of a) WST_0 blend; b) CHM_10 blend; c) MRB_10 blend

Figure 4. XRD pattern of clinkers: WST_0 1300 °C (black line), WST_0 1390 °C (red line), CHM_2.5 1390 °C (blue line) and MRB_2.5 1390 °C (green line)

Figure 5. Optical observation of polished clinker sections (etched with nital 2 %), of a) WST_0 1390 °C at 200X; b) CHM_2.5 1390 °C at 200X; c) MRB_2.5 1390 °C at 200X; d) WST_0 1390 °C at 500X; e) CHM_2.5 1390 °C at 500X; f) MRB_2.5 1390 °C at 500X

Table 1. Chemical composition (XRF, wt.%) of wastes and raw materials

Table 2. Targeted compositions for the blends, wt.%

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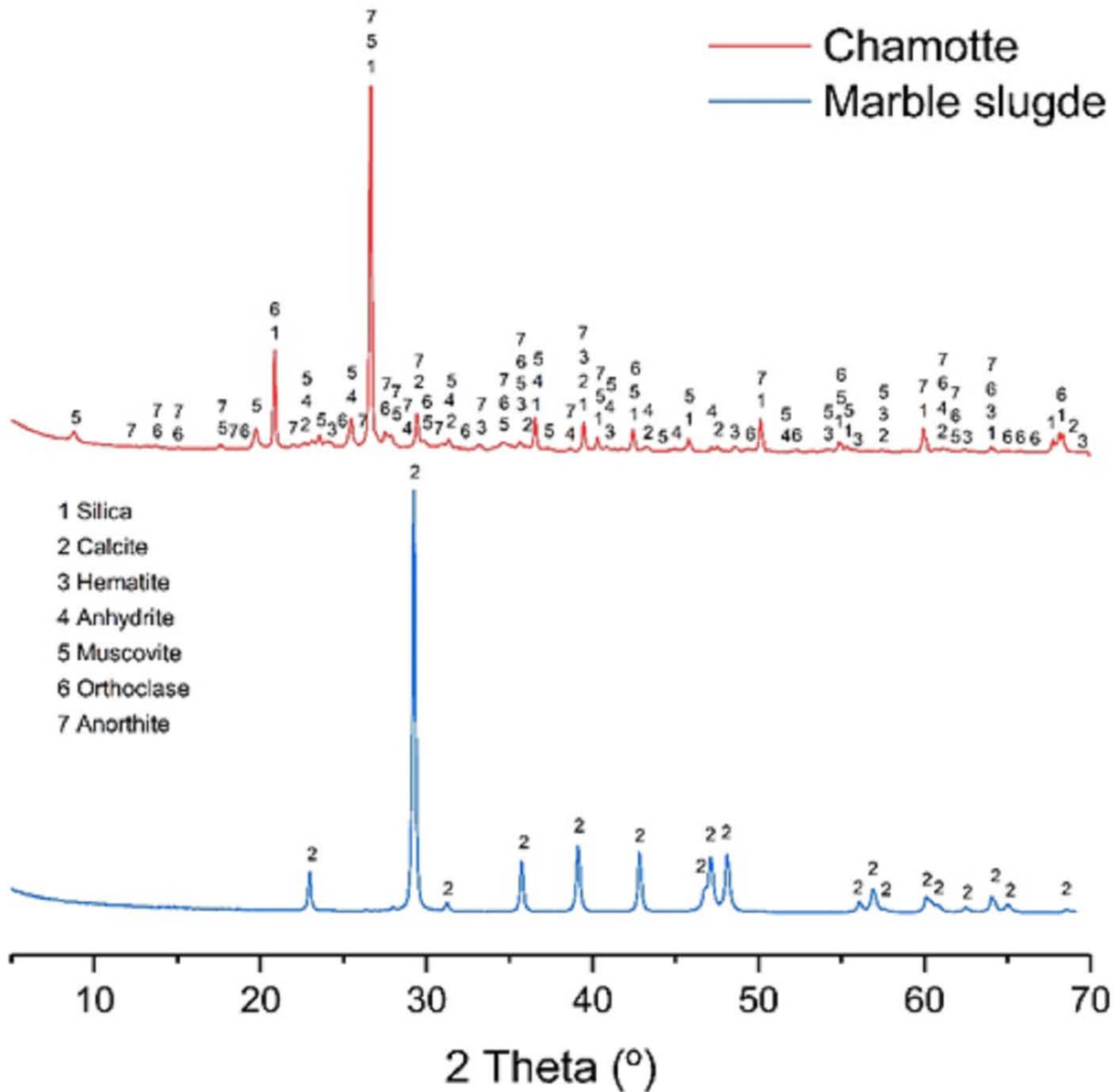
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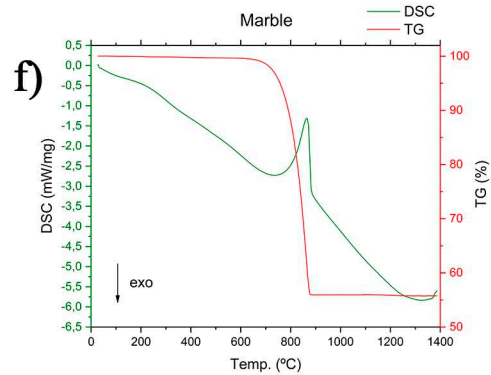
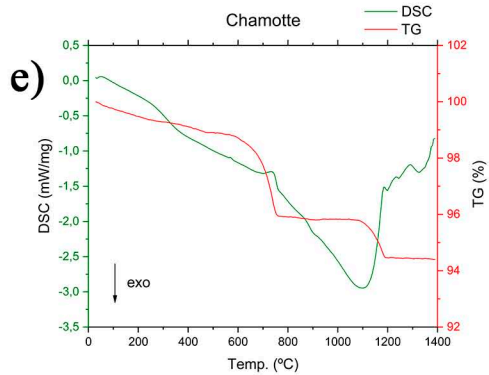
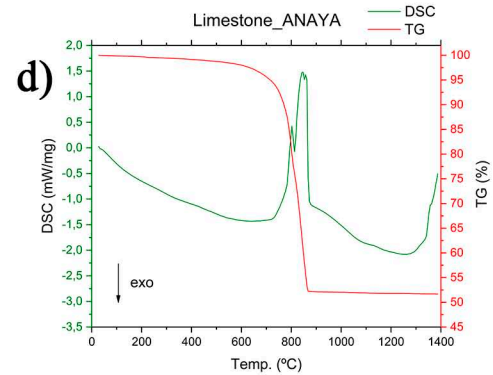
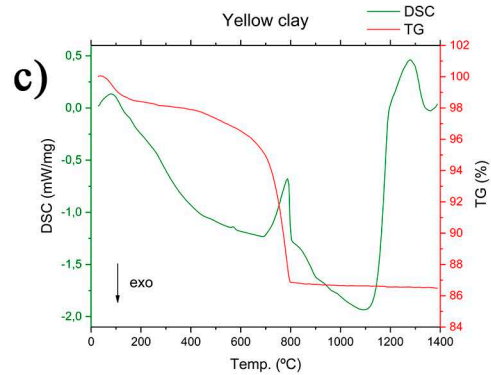
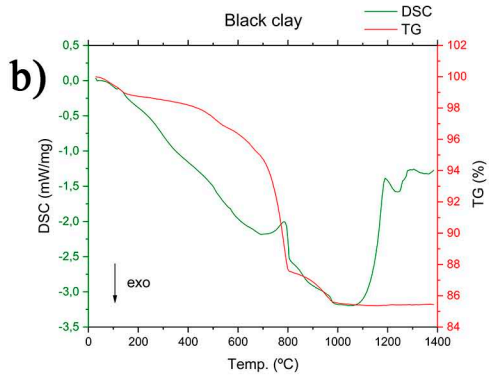
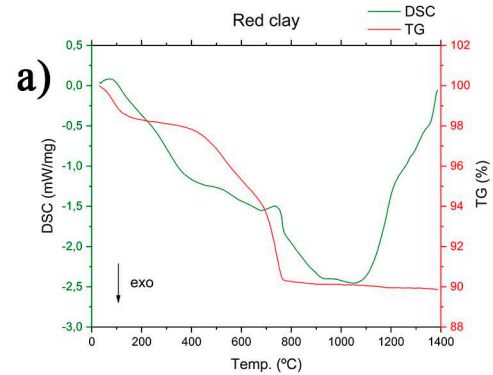
Table 1. Chemical composition (XRF, wt.%) of wastes and raw materials

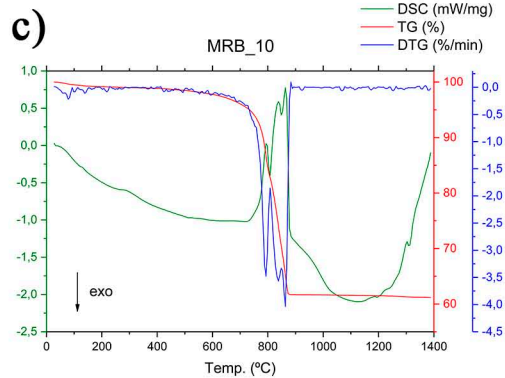
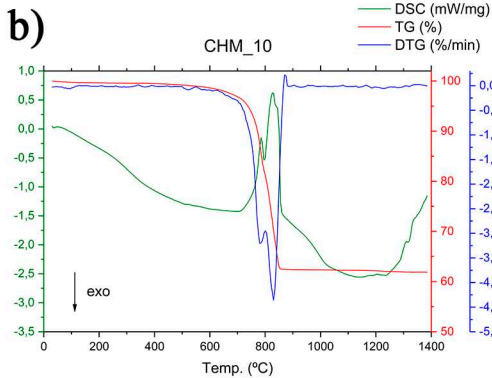
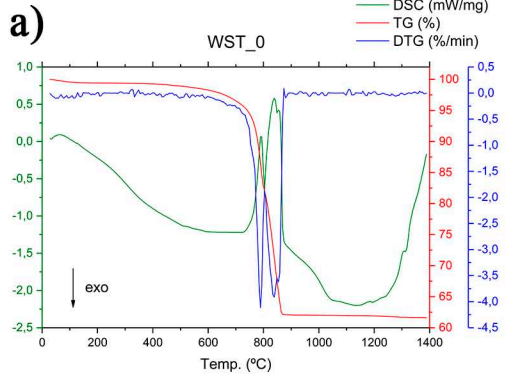
| Material | Al ₂ O ₃ | CaO | SiO ₂ | Fe ₂ O ₃ | Na ₂ O | K ₂ O | MgO | SO ₃ | TiO ₂ | LOI |
|---------------|--------------------------------|-------|------------------|--------------------------------|-------------------|------------------|-------|-----------------|------------------|-------|
| Red clay | 19.81 | 3.89 | 48.69 | 7.71 | 0.22 | 5.47 | 3.43 | 0.05 | 0.80 | 9.07 |
| Black clay | 10.96 | 17.41 | 44.29 | 5.56 | 0.40 | 2.92 | 1.79 | 8.26 | 0.65 | 10.70 |
| Yellow clay | 10.53 | 17.30 | 48.60 | 5.33 | 0.40 | 2.30 | 1.86 | 0.09 | 0.64 | 12.23 |
| Limestone | 0.00 | 34.54 | 0.00 | 0.26 | 0.00 | 0.01 | 19.12 | 0.02 | 0.02 | 46.31 |
| Chamotte | 13.75 | 14.75 | 51.23 | 6.92 | 0.43 | 3.11 | 2.38 | 3.63 | 0.72 | 4.00 |
| Marble sludge | 0.00 | 52.14 | 0.00 | 0.06 | 0.00 | 0.00 | 0.12 | 0.20 | 0.01 | 43.30 |

Table 2. Targeted compositions for the blends, wt. %

| Target | C ₃ S | C ₂ S | C ₃ A | C ₄ AF | Total | LSF | AM | SM |
|---------|------------------|------------------|------------------|-------------------|-------|-------|------|------|
| WST_0 | 11.32 | 62.73 | 14.22 | 11.73 | 100 | 78.0 | 2.03 | 2.13 |
| CMH_2.5 | 12.37 | 62.45 | 13.54 | 11.64 | 100 | 78.00 | 1.97 | 2.20 |
| CMH_5 | 13.10 | 62.27 | 13.04 | 11.59 | 100 | 78.00 | 1.93 | 2.26 |
| CMH_10 | 14.05 | 61.99 | 12.37 | 11.59 | 100 | 78.00 | 1.86 | 2.32 |
| MRB_2.5 | 11.03 | 62.83 | 14.39 | 11.75 | 100 | 77.99 | 2.04 | 2.11 |
| MRB_5 | 9.52 | 64.34 | 14.42 | 11.72 | 100 | 77.49 | 2.05 | 2.12 |
| MRB_10 | 10.54 | 62.74 | 15.01 | 11.71 | 100 | 78.11 | 2.11 | 2.06 |







- 1 Alite (C_3S)
- 2 Belite (C_2S)
- 3 Tricalcium aluminate (C_3A)
- 4 Tetracalcium aluminate ferrite (C_4AF)
- 5 Periclase
- 6 γ -Belite (γ - C_2S)

